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**CONTROLLED DECOMPOSITION AND OXIDATION -- A TREATMENT
METHOD FOR GASEOUS PROCESS EFFLUENTS**

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ABSTRACT

The safe disposal of effluent gases produced by the electronics industry deserves special attention. Due to the hazardous nature of many of the materials used, it is essential to control and treat the reactants and reactant by-products as they are exhausted from the process tool and prior to their release into the manufacturing facility's exhaust system and the atmosphere.

Controlled decomposition and oxidation (CDO) is one method of treating effluent gases from thin film deposition processes. This report discusses CDO equipment applications, field experience, and results of the use of CDO equipment and technological advances gained from field experiences.

INTRODUCTION

A number of extremely hazardous gases are routinely used by the semiconductor and photovoltaic industries to manufacture integrated circuits and other devices. Although the processes generally consume only small quantities of these gases, the nature of the gases is such that even small amounts of gas can do considerable damage to people and equipment in a very short time.

Effective controlled process exhaust gas conditioning has been and is becoming an issue of growing concern for specialty gas processors, process equipment manufacturers, users of process equipment various governmental agencies, insurance underwriters, and the general public.

CODES AND REGULATIONS

During the last few years, there has been and continues to be growing concern over finding safer methods of storing, dispensing, and monitoring these gases. More recently, the disposal of these gases has been receiving greater and greater attention.

In response to growing concern over toxic substance problems, Congress has enacted over two dozen regulatory statutes covering the routes by which certain chemicals or aspects of chemical use can threaten human health and the environment.

The laws are administrated by various federal regulatory agencies. The Occupational Safety and Health Administration (OSHA) has been given responsibility to insure a safe workplace. It sets mandatory job safety and health standards and provides reporting procedures for all industrial injuries and fatalities. The Environmental Protection Agency (EPA) attempts to prevent further poisoning of the environment by requiring industry to develop air quality control. The Federal Water Pollution Control Act dictates controls to improve water quality. The Toxic Substances Control Act regulates the use of certain toxic materials and establishes a toxic substance data base, while the Resource Conservation and Recovery Act gives EPA added authority over how waste materials are disposed.

The Department of Transportation sets standards for labeling (DOT Hazard System), packaging, testing, and handling compressed gases. Other agencies such as NIOSH (part of OSHA), the Uniform Building Code (UBC) and its companion document, the Uniform Fire Code (UFC), and other codes and state and local regulations have meaningful mandates that also deserve our attention.

The UBC published by the International Conference of Building Officials is the most widely used model building code in the country. It is the code for the western United States. The Basic/National Building Code is used primarily in the northeastern part of the country, and the Standard Building Code is used almost exclusively in the southeastern part of the country.

Occupancy is one of the primary regulatory criteria in the building code and is based on the use or occupancy in the proposed building. The seven major classes or Occupancy Groups are:

- A - Assembly
- B - Business
- E - Educational
- H - Hazardous
- I - Institutional
- M - Miscellaneous
- R - Residential

Within each of these Occupancy Groups are sub-categories called Divisions. In Group H Occupancy, there are six Divisions; and Division 6 may be briefly defined as semiconductor fabrication facilities.(2)

"Division 6. Semiconductor fabrication facilities and comparable research and development areas when the facilities in which hazardous production materials are used and constructed in accordance with Section 911 and when storage, handling, and use of hazardous materials is in accordance with the Fire Code." (2)

The UFC, which is the product of the Western Fire Chiefs Association, is a companion document to the UBC. Many provisions of the codes are interrelated and cross referenced. Administratively, the fire code is organized into eight basic parts consisting of one or more articles in each part. (4)

- Part I Administration
- Part II Definitions and Abbreviations
- Part III General Provisions for Fire Safety
- Part IV Special Occupancy Use

- Part V Special Processes
- Part VI Special Equipment
- Part VII Special Subjects
- Part VIII Appendices

Article 51 of the UFC, which is companion to H-6 of the UBC, appears in part V of the fire code. Article 51 deals with controls required for the utilization of hazardous materials in the production of semiconductor devices and related research functions. The required controls relate to the nature of materials encountered, their physical state, and the condition in which they are found in the building, i.e., storage, handling, or use. Control over the materials is achieved by limiting the amount of material in use at any particular work station and applying engineering controls such as sprinklers, automatic leak detection, local exhaust, and warning systems. (4)

The purpose of the UBC and UFC is to protect the public by regulating the construction, alteration, and maintenance of structures and the storage, handling, and use of hazardous materials. The codes establish certain minimum criteria that define the code intent. The UBC and UFC are concerned with fire and related hazards. The codes may be adopted locally or on a statewide basis. The adoption may be made by ordinance or by a legislative act.

An excellent reference concerning H-6 Occupancy is available through Larry Fluer, Inc., P.O. Box 10386, San Jose, CA 95157.

Two new pieces of "legislation" confronting the semiconductor wafer fabrication industry and other institutions using hazardous materials are:

1. Uniform Fire Code - Article 80 Rewrite
2. California Assembly Bill #1021

Previously the codes primarily addressed the storage, dispensing, and monitoring of hazardous materials. With the addition of Article 80, the codes now address STORAGE, DISPENSING, MONITORING, and DISPOSAL.

CONTROLLED PROCESS EXHAUST GAS CONDITIONING

Effective controlled process exhaust gas conditioning has been and is becoming an issue of growing concern for specialty gas processors, process equipment manufacturers, users of process equipment, various governmental agencies, insurance underwriters, and the general public.

Exhaust gas conditioning or removing harmful substances from process exhaust gases is not necessarily needed for successful device wafer fabrication; and perhaps since exhaust gas conditioning equipment is not revenue producing, its importance has not been previously fully acknowledged. However, Factory Mutual, a leading insurance company for semiconductor manufacturers, reports \$60,000,000 in claims were paid for 112 incidents from 1974 through 1986. The \$60,000,000 reported by Factory Mutual does not include claims covered by other underwriters, unreported losses, and self-insured claims. Fire was by far the most frequent cause of loss

and the ignition of flammable and pyrophoric gases was the leading cause of fire. Hydrogen and silane gases were involved in approximately 90 percent of the reported incidents.

Table I: SEMICONDUCTOR PLANT LOSSES
1974 THROUGH 1986 \$60,000,000

<u>CAUSE</u>	<u>NUMBER OF INCIDENTS</u>
Fire	72
Liquid Leakage or Spillage	29
Human Element	11
TOTAL	112

Table II: CAUSES OF FIRES AT SEMICONDUCTOR PLANTS

<u>CAUSE</u>	<u>NUMBER OF INCIDENTS</u>
Ignition of Flammable or Pyrophoric Gases (27 of the 29 or approximately 90% involved Hydrogen or Silane)	19
Electrical Origin	20
Immersion Heaters	13
Ignition of Flammable Liquids	6
Hot Plates	4
TOTAL	72

Although exhaust gas conditioning may not be essential for semiconductor wafer fabrication, it is important for the protection of personnel, protection of the environment, and, as stated above, the protection of the manufacturing facility.

The contaminants encountered in process exhaust gas streams are extremely varied. Rarely does an exhaust stream contain only one classification of contaminant -- whether it be particulate, gas, or vapor. While the gases introduced into almost all semiconductor wafer fabrication processing chambers are well defined, the composition of the gas mixture exiting the process chamber is generally not precisely defined. Furthermore, since the mid 1970's, there has been an ever increasing utilization of subatmospheric or reduced pressure (vacuum) processing in semiconductor wafer fabrication. This has introduced additional unknowns such as pump oil vapors into the process effluent.

For the most part, reactive gases are not released unreacted from a process chamber; and in most cases, the gases are present only in low concentrations. However, almost all are highly toxic (AsH_3 , PH_3 , B_2H_6), pyrophoric (SiH_4), flammable (H_2), or corrosive (HCl). Hydrogen (H_2) is a by-product of all hydride (SiH_4 , AsH_3 , B_2H_6 , PH_3) reactions; and under controlled exhaust conditions, SiH_4 can be the ignition source for a serious H_2 reaction.

"THE PENINSULA TIMES TRIBUNE

DAMAGE MAY RUN HIGH IN FIRE A LOCAL PLANT
MOUNTAIN VIEW -

...The fire, ignited by gas and vaporized oil, spread through an air duct system in a fabrication room where valuable silicon chips are manufactured.

...The fire began in an air duct system where vaporized oil from a vacuum pump and gas from a malfunctioning reactor had collected."

No manufacturer wants a mishap due to improperly handled exhaust gases to end up in the morning paper.

In the past, dilution or simple water washing was employed to dispose of exhaust gases. Dilution to "safe" levels has long been an accepted practice, but public sentiment and new codes are diametrically opposed to any practice in which chemicals of any kind are released into the atmosphere untreated.

Conscientiously, we should address pounds per hour, not parts per million (ppm).

"DILUTION IS NO SOLUTION TO POLLUTION!"

Plain water scrubbing is ineffective for most of the hazardous gases encountered in wafer fabrication.

SOURCE VS. CENTRAL EXHAUST GAS CONDITIONING

Exhaust gas conditioning equipment may be divided into two broad categories -- source and central systems.

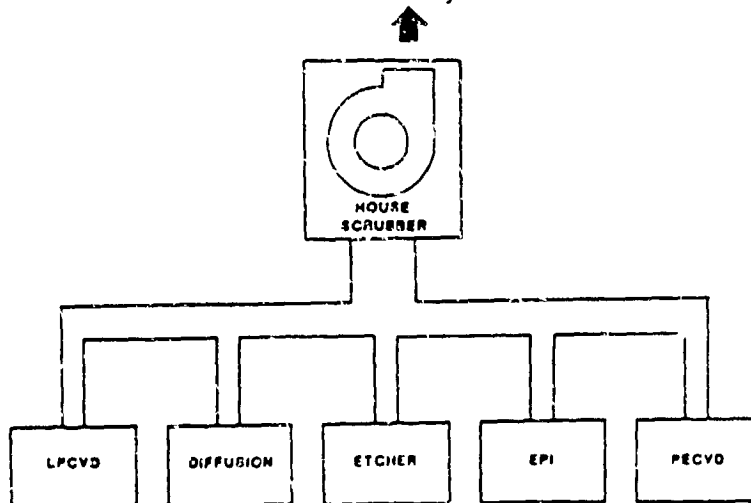


Fig. 1. Central Conditioning - Multi process tools with incompatible exhaust effluent entering common duct system and being transported to remotely located exhaust treatment system.

Because of the nature and low volume of effluent exiting most wafer fabrication systems, it is desirable and more effective to condition process exhaust gases as close to their source as is physically possible.

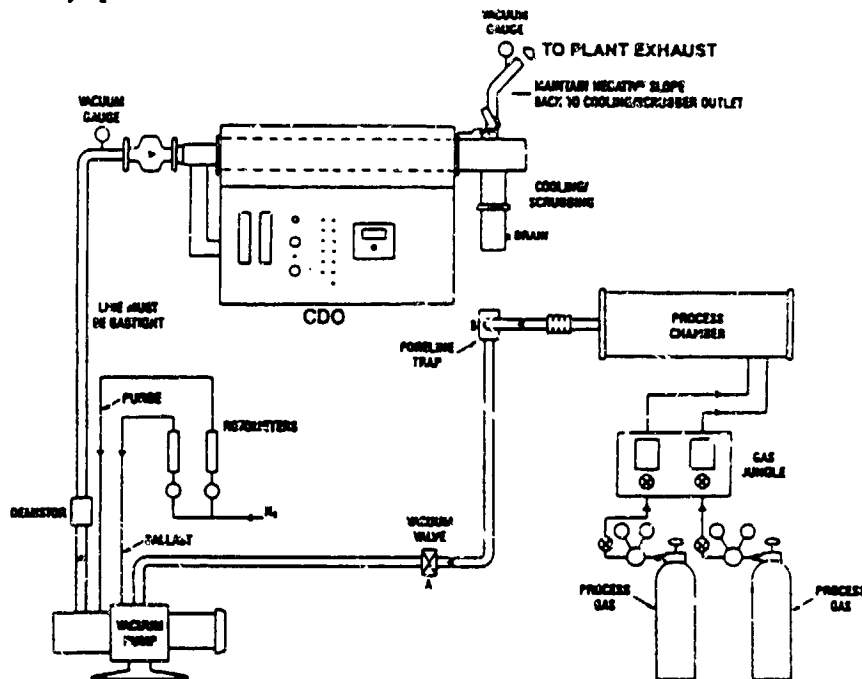


Fig. 2. Source Conditioning - Dedicated gas treatment system located as close to process tool exhaust as physically possible.

Because of the nature of the gases and vapors exiting most process systems and based on the interpretation of codes and regulations, source conditioning may be mandatory in the future. From UFC Article 51: "Duct Systems - Reactives. Two or more operations shall not be connected to the same exhaust system when either one or the combination of the substances may constitute a fire, explosion, or chemical reaction hazard within the duct system." (4)

Also, Section 1105 of the 1985 Edition of the Uniform Mechanical Code: "A mechanical ventilation or exhaust system shall be installed to control, capture, and remove emissions generated from product use or handling when required by the Building Code or Fire Code and when such emissions result in a hazard to life or property. The design of the system shall be such that the emissions are confined to the area in which they are generated by air currents, hoods, or enclosures, and shall be exhausted by a duct system to a safe location or treated by removing contaminants. Ducts conveying explosives or flammable vapors, fumes, or dusts shall extend directly to the exterior of the building without entering other spaces. Separate and distinct systems shall be provided for incompatible materials."

CONTROLLED "SOURCE" PROCESS EXHAUST GAS CONDITIONING IS:

1. THE WAVE OF THE FUTURE
2. EVOLUTIONARY/EVOLVING
3. MORE EFFECTIVE
4. DESIRABLE
5. SAFER
6. ESSENTIAL TO COMPLY WITH CODES

PROCESS TOOL EXHAUST

Many of the process systems in use today and proposed for the future are sub-atmospheric pressure systems utilizing vacuum pumps.

The required pumping systems for sub-atmospheric processes are fairly well defined and for simplicity may be broken down into three areas (see Fig.1): foreline (inlet), pump, and exhaust.

That portion of the pumping system connecting the process chamber to the vacuum pump may be called the foreline or inlet. The foreline generally includes a flexible stainless steel interconnect line, a particulate trap, and a vacuum valve. Pumping precautions which should be taken include:

- (a) preventing the condensation or trapping of chemicals in the pump rotor and stator area;
- (b) preventing oxygen from entering the pump (i.e., through the ballast valve);
- (c) preventing the accumulation of explosive, toxic, and/or corrosive gases in the dead volume of the pump oil reservoir.

Items (a) and (b) may be accomplished by injecting a 1 to 2 SLM dry nitrogen flow into the pump ballast inlet. Since most pumps are equipped with an inlet to the pump oil chamber, item (c) may be accomplished by flowing 2 to 3 SLM of dry nitrogen into this inlet. Another effective technique for the oil chamber purge is to bubble the dry nitrogen through the pump oil. This dry nitrogen flow will help to dilute and eject the explosive, toxic and/or corrosive gases from the pump oil chamber. Ideally, regulators, flow meters, and pressure gauges should be used to set and monitor the dry nitrogen gas flow.

It should be noted that large flows of purge gas through the oil chamber may result in an unreasonable loss of fluid from the pump due to rapid removal of fluid vapor. Excessive nitrogen purge may also dilute the exhaust gases to such a diluted concentration as to be detrimental to effective exhaust gas conditioning.

The effluent exiting the pump casing frequently contains pump fluid vapors and toxic and flammable or explosive gases. An uncontrolled mixing of the reactive gases (i.e., silane or hydrogen) with air can create explosive conditions. Uncontrolled discharge of toxic gases (i.e., arsine, diborane, and phosphine) can create environmental as well as personnel hazards. Unconditioned vacuum pump fluid vapors can condense in exhaust ducting causing maintenance and health and safety hazards.

The toxicity and flammability of vacuum pump effluent is hazardous enough that particular attention should be given to "gas-tightness" of the entire high pressure (exhaust) section and to the "conditioning" or treatment of the pump effluent prior to its release into the atmosphere.

The design of the gas exhaust line mounted on the discharge port of a mechanical pump should follow certain basic rules (see Fig.2):

- a) Exhaust lines should be sized so as not to create pump discharge back pressure.
- b) The exhaust line should be constructed of gas tight metal tubing. Stove pipe type 'jointed' ducting should not be used as it is not air tight. Air must not be allowed to mix with the gases prior to conditioning.
- c) The line should have slightly sub-atmospheric pressure ($\frac{1}{2}$ inch to 1 inch of water below atmosphere) to assist in ejecting the effluent. However, this pressure should not be so low (i.e., 8 to 9 negative inches of water) that excessive pump oil vapors are sucked from the pump.
- d) A pressure gauge should be installed on or just downstream of the pump exhaust port to monitor exhaust line pressure.
- e) The exhaust line should incorporate a device to condense fluid vapors from the pump effluent.
- f) "Conditioning" of the pump effluent is necessary for personnel safety, protection of property, and protection of the environment.
- g) Pressure (vacuum) gauges should be mounted on the inlet and discharge sides of the conditioning equipment.

While the gases introduced into the process chamber are generally well known, the composition of the gas mixture exiting the process chamber, passing through, and exiting the pump is generally not precisely defined. However, the pump effluent generally contains enough toxic, explosive, and combustible materials that effluent "conditioning" is essential

TABLE III: TYPICAL SUBATMOSPHERIC CVD GASS EFFLUENT

<u>CVD PROCESS</u>	<u>PROCESS GASES</u>	<u>PROCESS EFFLUENT</u>
Poly	SiH_4	Si, SiH_4 , H_2 , Pump Fluid Vapors
Doped Poly	SiH_4 , PH_3	Si, SiH_4 , PH_3 , H_2 Pump Fluid Vapors
Low Temperature Oxide (400°C)	SiH_4 , O_2 , PH_3	SiO_2 , SiH_4 , O_2 , PH_3 , H_2 , Pump Fluid Vapors
Tungsten? Tungsten Silicide	SiH_4 , WF_6 , H_2	WF_6 , Wx , SiH_4 , SiHx , H_2 , N_2 , Pump Fluid Vapors

PROCESS EXHAUST GAS CONDITIONING

Controlled combustion is a method of reducing the toxic and flammable hazards of vacuum pump effluent.

Process exhaust gases enter the Controlled Combustion, Decomposition, Oxidation (CDOIM) System (see Fig. 3) through the unit's flame check and under controlled conditions are mixed with an oxygen source in the oxygenator. The oxygen enriched gases then flow through a high temperature section where combustion takes place and exit the CDOIM System through a water mist cooling and scrubber section. Tases and pump oil vapors are combusted and oxidized.

In the CDOIM unit, the pump effluent is oxygen enriched under controlled conditions and exposed to a high temperature environment thereby increasing the likelihood of a complete chemical reaction.

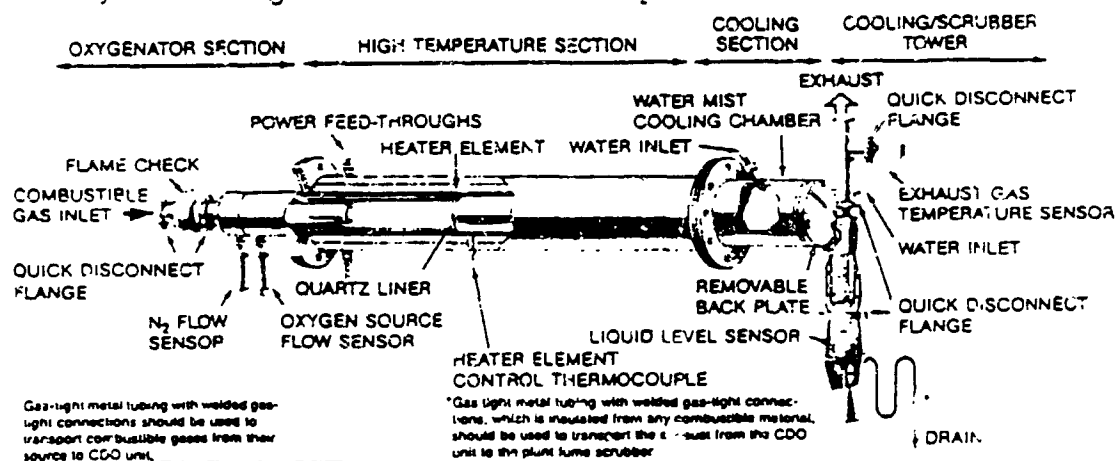


Fig 3. Controlled Combustion, Decomposition, and Oxidation System Cross Section

Control of time, temperature, turbulence, and oxygen is essential for complete reaction. Time is the period of residence of the waste gas(es) in the combustion chamber. Time is a function of combustion chamber length and diameter and gas volume.

Temperature is the temperature of the waste gas(es) in the combustion chamber. Turbulence is necessary to insure the proper mixing of the waste gas(es) and the oxygen source. Oxygen is required to support the complete reaction of the waste gas(es).

As reported by Arco Solar, Inc. in their January, 1937, "Evaluation of Hazards Associated With the Manufacture of Thin Film Solar Cells for Brookhaven National Laboratory": "The CDO approach has been shown to be highly effective in the controlled combustion of silane and diborane, the results suggesting performancy efficiency approaching 100% for silane. However, under the defined operating conditions, the system appears less efficient in the removal of phosphine." (11)

Since publication of the Arco report, Innovative Engineering Inc. has performed extensive testing with arsine, diborane, and phosphine.

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